EVALUATION OF CONDUCTIVITY, INTERFACIAL PROPERTIES AND MICELLIZATION BEHAVIOUR OF IMIDAZOLIUM GEMINI SURFACTANTS

SYNOPSIS

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By

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1. Title: EVALUATION OF CONDUCTIVITY, INTERFACIAL PROPERTIES AND MICELLIZATION BEHAVIOUR OF IMIDAZOLIUM GEMINI SURFACTANTS

2. Introduction

In nearly each and every industrial field and day-to day life, surfactants are broadly utilized (Das et al 2014). Surfactants are also known as surface-active agents, having the potential to lower the interfacial or surface tension between two liquids (Kalam et al 2019, Nagtode et al 2023). The non-polar tail group of surface-active agents is adaptable with oil and on the other hand polar head is compatible with water (Kanduc et al 2023). Due to the amphiphilic nature of surfactants, several properties arise in solution like self-aggregation called micelles which is simplest aggregated form and the lowest concentration where this phenomenon occurs commonly known by Critical Micelle Concentration (CMC) (Banjare et al 2017, Das et al 2013). These are cost-effective, have high rising physico-chemical usage and can be used for hygienic development of society, as a result their usage is growing 3-4% in industry (Sharma et al 2023). The potency of the surfactants is governed by its ability to lowering the surface tension and if a surfactant can reduce the water surface tension from 72 to 30mN/m and interfacial tension from 40 to 1mN/m against n-hexadecane, then it is said to be a good surfactant (De et al 2015). The hydrophobic interactions between alkyl chain lengths and electrostatic repulsions among the head groups managed the arrangement of the aggregates of surfactants (Hu et al 2020).

The annual manufacturing quantity of cationic surfactants rises to 350,000- 500,000 tons. Because of their devastating activity along with emulsification properties, these surfactants are repellent to some amount of biological agents and undergo slow

biodegradation (Patial et al 2014). The synthesis of cationic surfactants is not complicated and due to this, these are attracting specific attentiveness (Jia et al 2009).

The various forms of Pyridinium, imidazolium, piperidinium as well as pyrrolidinium cationic surfactants have been investigated and studied (Hilal et al 2021). Optimistic results in both conventional and modern fields of imidazolium surfactants in correlation with cationic surfactants have revealed. Favourable results of imidazolium surfactants have illustrated associated use of cationic surfactants in advance application as well as conventional field. Also the imidazolium surfactants found to be finer than standard quaternary ammonium surfactants in various cases. These surfactants have showed superb potential to form extensive variety of complex like drug and protein molecules and nucleic acids (Bhadani et al 2016).

Mono-cationic surfactants of imidazole have been synthesized with an ester group inserted between imidazole and hydrocarbon chain (Sunitha et al 2011). These are extensively important in health and individual care material, mineral and petroleum dispensation, biological process, safety of foods and crop (Schramm et al 2003). Imidazolium surfactants predominantly are significant molecule utilized as the corrosion inhibitors, in dispensation of yard goods as well as suspension polymerization for the flotation of natural resources (Ahmad et al 2014).

One of the fascinating classes of surfactants or recently discovered stage of amphipathic molecules which comprise of two monomeric surfactants joined chemically using rigid or flexible spacer at the head groups are gemini surfactants (Kumar and Tyagi 2014, Ao et al 2011). Gemini surfactants show full of promise usage in the area of skin care, treatment, biological science, making of porous materials and petrochemicals etc. (Ao et al 2008). These surfactants exhibit better antimicrobial activity in case of viruses, fungi, yeasts and bacteria (Tawfik 2015). One of the worthwhile properties of surfactants is low penetration on skin and it is due to the high molecular weight of gemini surfactants which makes them popular in the body care products like shampoos, soaps and cosmetics (Patil et al 2016).

In contrast to monomer, these surfactants have superior surface acting properties, quick biodegradability, and well-built affinity with cell membrane of bilayer phospholipid and stronger interaction with metal surface (Zhu et al 2021). In view of the fact that gemini surfactants have usage in extensive areas like indigenous materials in cosmetics, detergents, individual care products, additives for coatings as well as paints, biocides, organic synthesis, material chemistry, nanotechnology, improved oil recovery and numerous life branches etc.

owing to their special properties (Cao et al 2021). The considerable homogenous catalytic reactions accompanied by emulsification, solubilisation including countless applications in industries like gene transfection, corrosion inhibitors, industrial detergency and micellar catalysis are the uses of gemini surfactants because of their unique properties (Zhang et al 2017).

The imidazolium gemini surfactants by virtue of the presence of two imidazolium head groups, have shown multiple advantages in comparison with imidazolium monomeric surfactants as these surfactants exhibit stronger tendency to form self-aggregation. Imidazolium gemini surfactants could be utilized as supramolecular templates to synthesize a variety of functional materials (Zhou and Antonietti 2004). In latest years, a number of novel gemini/dimeric surfactants have been synthesized and examined extensively (Wang et al 2014, Sharma et al 2020, Shaheen et al 2020).

Keeping in view the above information, present investigation has been taken with the following objectives:

1. Synthesis and characterization of imidazolium based gemini surfactants
2. Evaluation of thermal stability of synthesized compounds
3. Investigation of conductance, surface active properties and interaction behaviour of synthesized compounds with appropriate solvent
4. Determination of thermodynamic properties for micellization behaviour of synthesized surfactants.

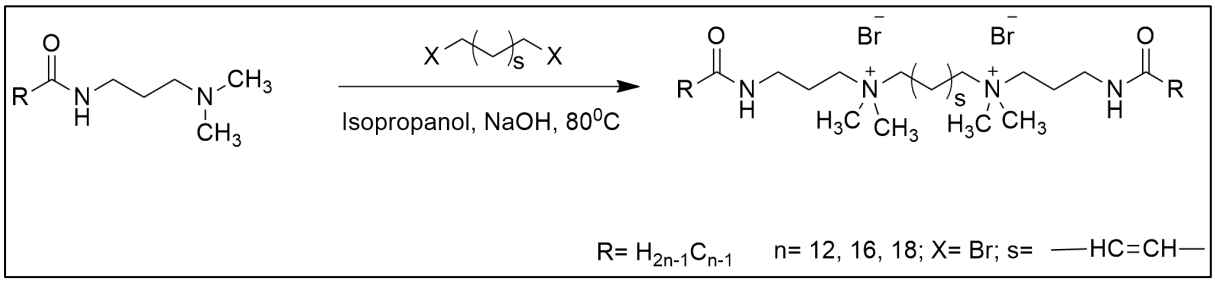
3. Expected new knowledge

- The purity and yields of synthesized surfactants would be measured by fundamental analysis like spectral techniques.
- Thermogravimetric analysis would provide the information for thermal stability of synthesized compounds.
- The results obtained from conductivity measurement would be used to study micellization behavior, nature of surfactants (whether strong or weak electrolytes), degree of dissociation and thermodynamics of micellization.
- Surface active properties would provide the data about surface parameters i.e., surface area occupied by molecule at interface, surface excess concentration, effectiveness of surface tension reduction and Critical Micellar Concentration.

4. Review of literature

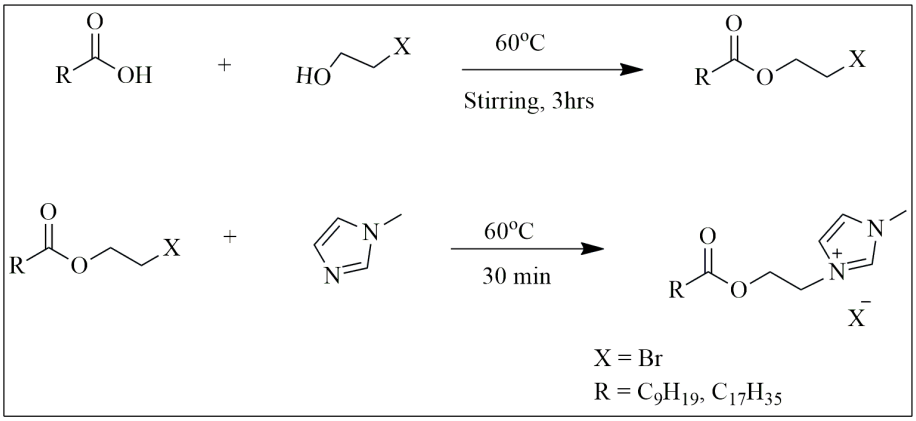
Pyridinium, pyrrolidinium, piperidinium, amino acid-based, and imidazolium gemini surfactants are among the novel families of cationic gemini surfactants that have been synthesized and studied (Sharma et al 2017). However, because of their inherent qualities, possible uses, and strong head group polarizability to form self-aggregated assembly, imidazolium-based gemini surfactants are attracting the attention of researchers (Vyas et al 2019, Garcia et al 2013).

Yang et al (2021) synthesized new class of amide gemini surfactants. First of all, 1, 4-dibromo-2-butene was mixed with 100 ml of isopropanol and then, propyl dimethyl amine was added and stirred the reaction for 24 hrs at 80˚C where sodium hydroxide used as a catalyst to form desired gemini surfactants with non-identical chain lengths (Scheme 1). The determination of the synthesized structures was done by FT-IR and ^{1}H-NMR. Conductivity and surface tension measurements have been calculated. The interfacial tension, antistatic, aggregates and antimicrobial activities were also measured and it is observed that on increasing chain length, the adsorption on interface decreases. The values of CMC decrease with the elongation of alkyl chain length (Yang et al 2021).



Scheme 1

Sharma et al (2020) synthesized cationic monomeric imidazolium surfactants based on renewable raw materials. The synthesis occurred in two step reaction. First of all, the fatty acid was treated with halogenated alcohol in the presence of sulphuric acid and stirred at 60˚C for 3 hrs and after work-up of the crude desired esters were obtained. The esters were then reacted with calculated amount of 1-methyl imidazole at 60˚C for 30 min to get the desired monomeric surfactants (Scheme 2). The purity of synthesized compounds was checked by ^{1}H- NMR, FTIR and TGA. Moreover, thermodynamic parameters have also been evaluated using conductivity measurements and showed that micellization process is more favourable than dissociation process. Surface-active properties indicated that synthesized molecules have aptness to constitute micelles in the solution and therefore can adsorb at air-water interface (Sharma et al 2020).



Scheme 2

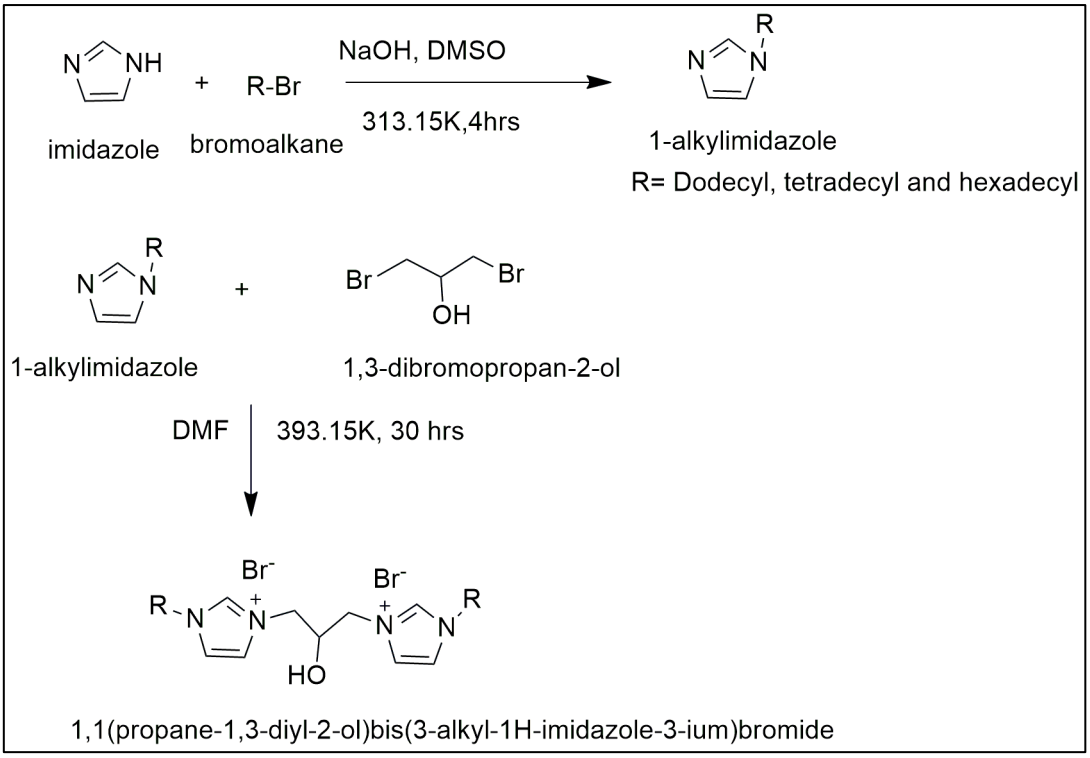
Shaheen et al (2020) reported chain of gemini surfactants based on imidazole using different hydrocarbon chain length and spacer having hydroxyl group. The compounds were synthesized in two step reaction. The very first step involved the reaction of imidazole with 1- Bromododecane in the presence of DMSO and NaOH at 313.15 K for 4 hrs to get the intermediate product named 1-alkylimidazole. Furthermore, in the second step 1-alkylimidazole reacted with spacer containing hydroxyl group i.e., 1, 3-dibromopropan-2-ol and DMF at 393.15 K for 30 hrs and crude solid compound was obtained which was further crystallized (Scheme 3). The compounds were then identified by ^{1}H-NMR, ^{13}C-NMR, FTIR and mass spectroscopies. After that, CMC was calculated by means of conductivity and surface tension parameters and the data revealed that CMC value of the synthesized gemini surfactants decrease as the hydrophobic chain length increase. Moreover, counter binding constant, thermodynamics and cytotoxic properties have also been calculated (Shaheen et al 2020).

Gawali and Usmani (2019) synthesized cationic gemini surfactants from triethylenetetraamine. Initially, triethylenetetraamine was reacted with different fatty acids at 140˚C for at least 1 hour to give amides. The cyclization of amides was done by heating constantly for 3.5 hrs at 180-200˚C which results in the formation of 2-alkyl-1-diethylenediaminimidazoline. In next step, synthesized intermediate was then reacted with spacer in the presence of catalyst KOH and tetra butyl ammonium iodide at 80˚C in ethanol as solvent. The mixture was stirred for 36 hrs and the desired cationic gemini surfactants were obtained (Scheme 4). The structures of the synthesized surfactants were analysed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopies. Surface tension, wetting power, stability of emulsion and dispersion ability was also checked and they have capability to lower surface

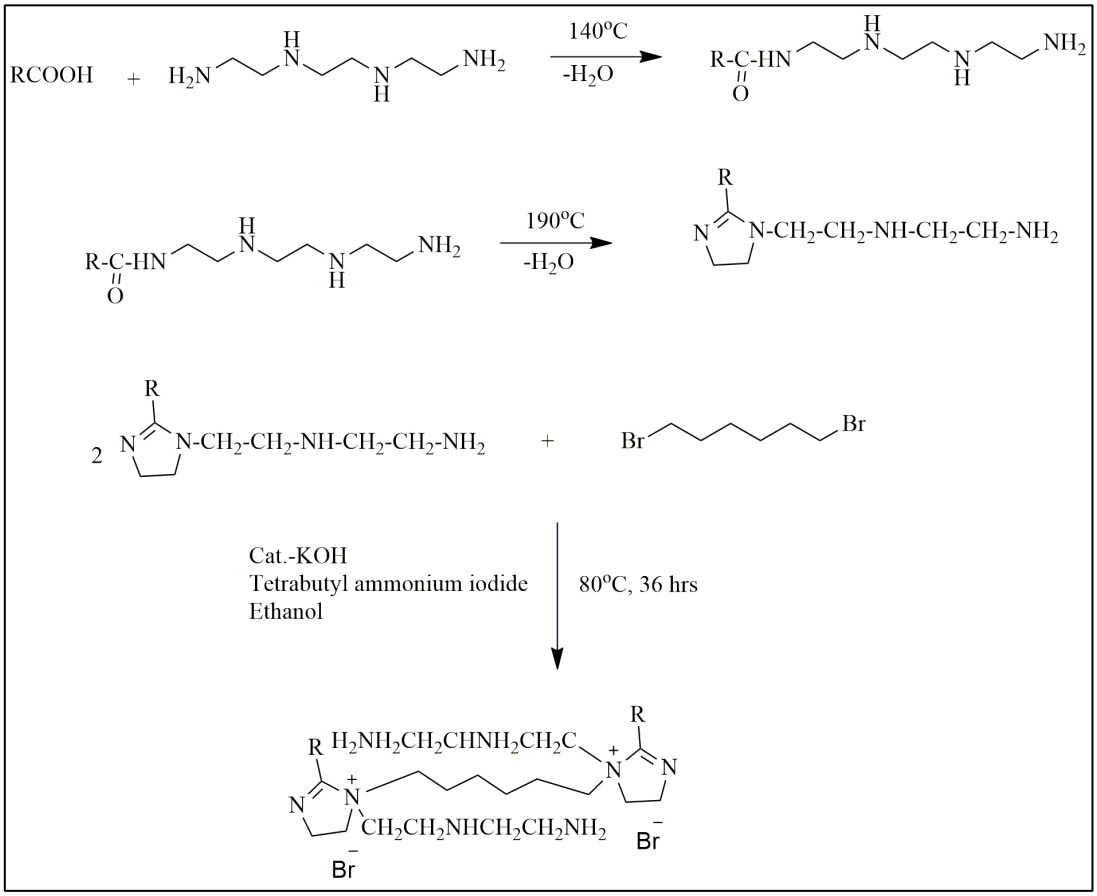
tension. Degradation behaviour, antimicrobial activity and corrosion inhibition efficiency was also determined (Gawali and Usmani 2019).

Lei et al (2019) synthesized a latest series of imidazolium gemini surfactants (ionic-liquids) with different series. 1-alkyl imidazole along with DMF was added in a flask under nitrogen atmosphere and then 1, 3-dichloropropan-2-ol was added to the same flask with 50 ml of DMF as solvent. The mixture was refluxed for 28 hrs at 120˚C. Moreover, solvent was removed using rota evaporator and then recrystallized using chloroform and mixed solution of an ethyl acetate (Scheme 5). The colour of the synthesized compounds was white. Furthermore, the compounds were analysed by ^{1}H- NMR and thermogravimetric analysis has also been done. The adsorption behaviour has been measured using rheological properties (Lei et al 2019).

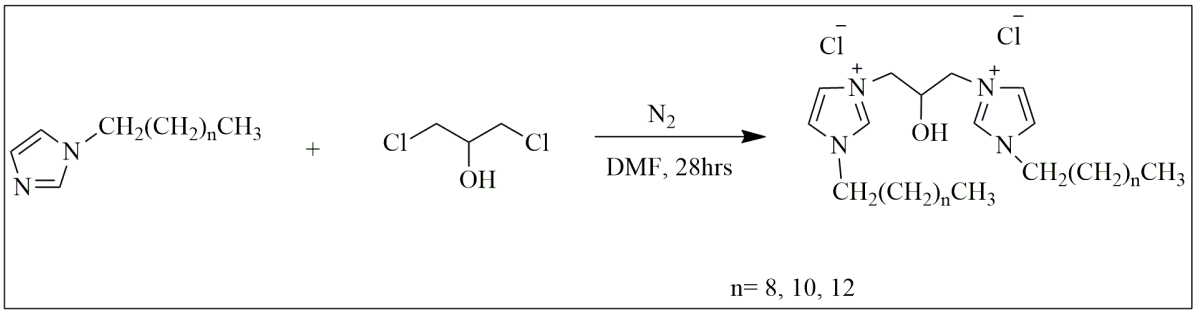
Heakal et al (2017) reported gemini surfactants accompanied by different spacer lengths. In the first step, imidazole was mixed with alkyl halide along with acetonitrile as solvent and refluxed for 3 hrs to form monomeric imidazolium surfactants. The product was then reacted with spacer of different chain lengths to form the desired gemini surfactants (Scheme 6). The synthesized compounds were then analysed using FT-IR, ^{1}H-NMR and mass spectrometry. Thermal stability was analysed using TGA. Furthermore, the inhibition property for corrosion has been measured using different methods and found that the synthesized gemini surfactants are good inhibitors of C-steel in oilfield water. Surface analysis i.e., SEM, EDX and FTIR confirmed that the surfactants can be adsorbed on C- steel surface (Heakal et al 2017).



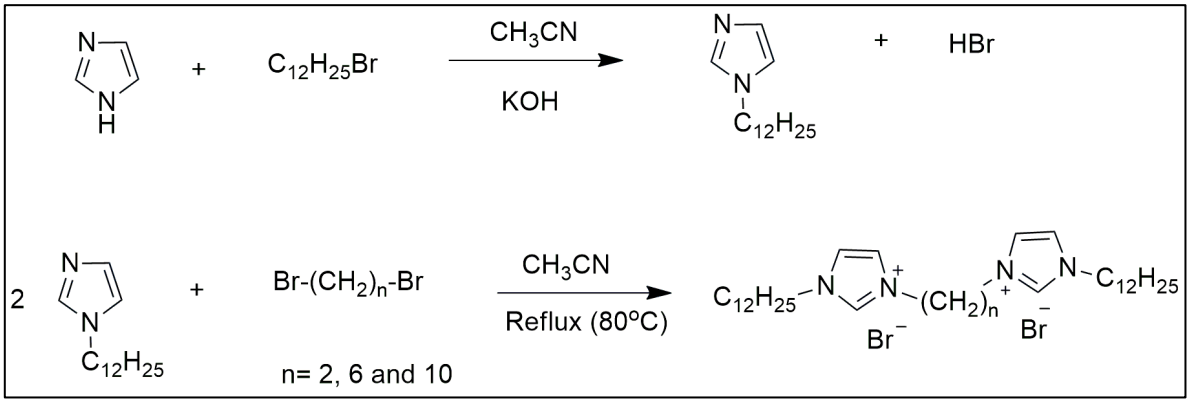
Scheme 3



Scheme 4

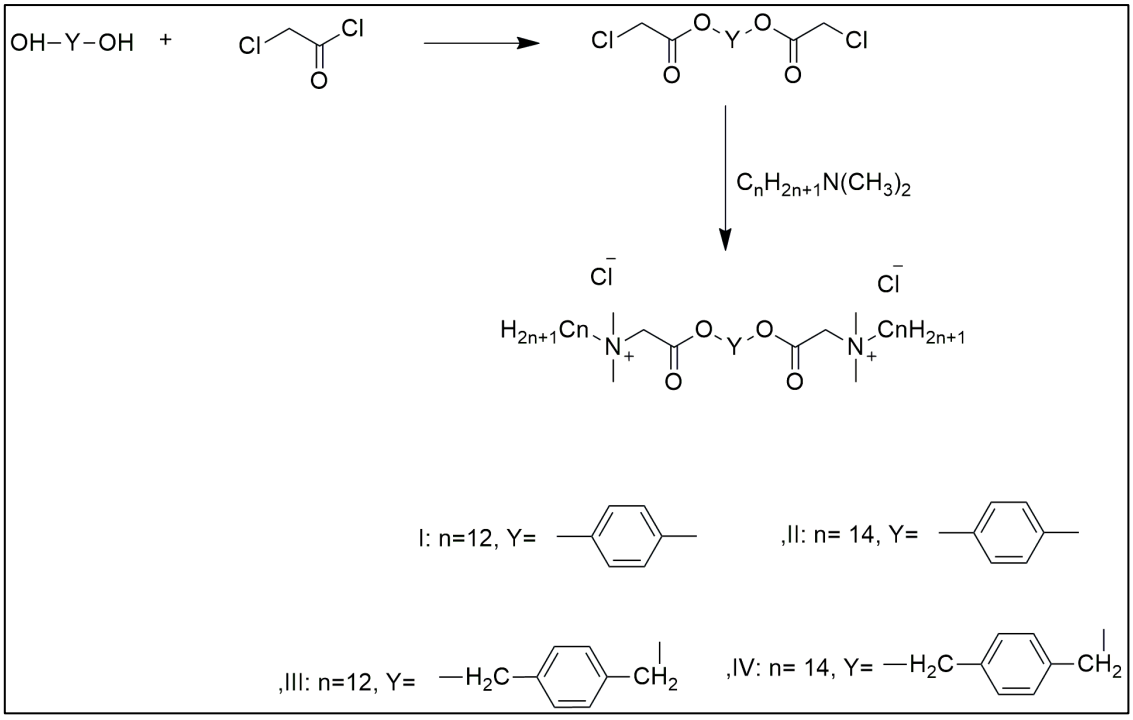


Scheme 5



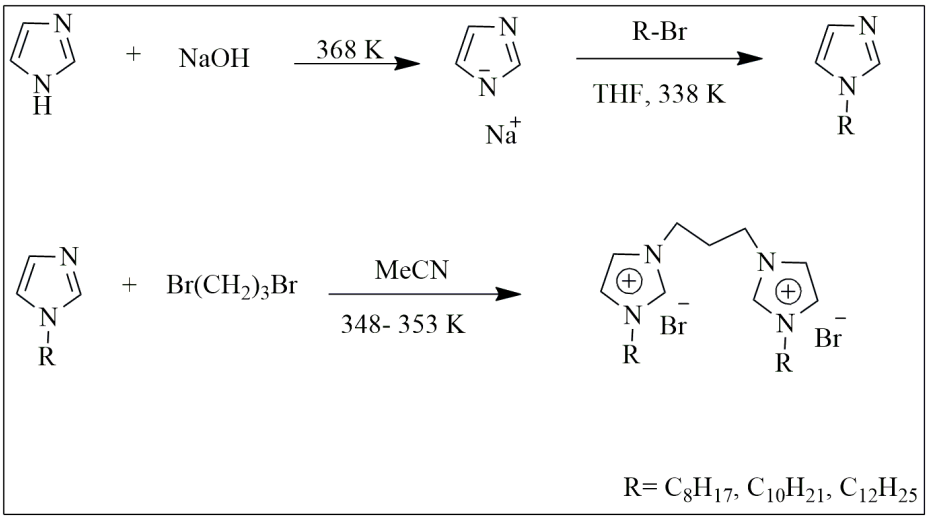
Scheme 6

Zhu et al (2016) synthesised cationic gemini surfactants with partly rigid spacers. 1, 4-benzene dimethanol was reacted with anhydrous dioxane at 0-5˚C. Then, triethylamine was added on to the mixture and then after complete separation of mixture, chloroacetyl chloride was added drop-by-drop and heated for 3 hrs at 30˚C and intermediate was formed. This intermediate was then dissolved in anhydrous dioxane. Moreover, the mixture was added with N, N- dimethyltetradecylamine and stirred under refluxing for 48 hrs and white coloured dimeric surfactants were obtained (Scheme 7). FT-IR, ^{1}H-NMR and ESI-MS techniques were used for analysis of structures of synthesized compounds. The surface-active properties were measured from conductivity and surface tension data. The CMC values obtained from the measurements decrease when hydrophobic chain length increases. Furthermore, thermodynamic parameters have also been calculated from conductivity results which show that micellization is spontaneous. Antimicrobial activities of compounds were superb against *E. coli* as well as *B. subtilis* and antimicrobial rate increase with rise in concentration (Zhu et al 2016).



Scheme 7

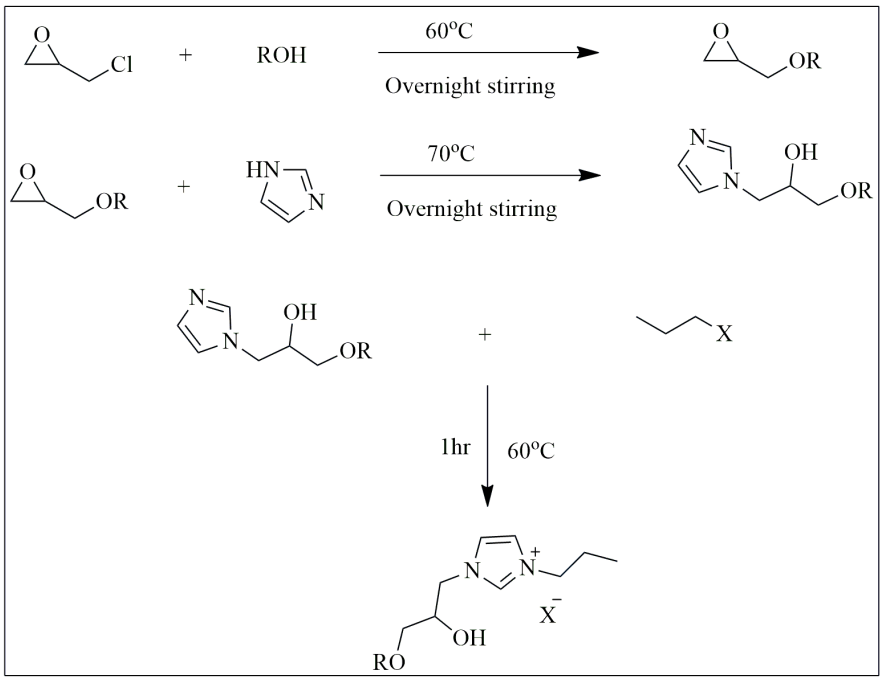
Ren et al (2015) synthesized a new class of imidazolium gemini surfactants. The synthesis took place in two step reaction. Firstly, Imidazole was melted in a flask and after that NaOH pellets were added to the RB flask. N-alkylimidazole was formed by stirring imidazole and NaOH in round bottom flask for 4hrs at 368 K. Work-up was done, also THF was added and again refluxed for 1 hr. Alkyl bromide was added drop-wise, the mixture was stirred for two days. Excess solvent was removed; formed N-alkylimidazole was recrystallized. In further step, N-alkylimidazole was treated with 1, 3 dibromopropane under nitrogen atmosphere at 348- 353K for 2 days where acetonitrile was used as solvent (Scheme 8). FT-IR, 1H-NMR and elemental analysis was done for the analysis of the synthesised surfactants. Moreover, surface tension parameters and conductivity measurements were used for the calculation of CMC values. As the hydrophobic chain length increase, CMC values decrease. The thermodynamic parameters have been calculated using phase separation model and results shown that the process of micellization was more spontaneous (Ren et al 2015).



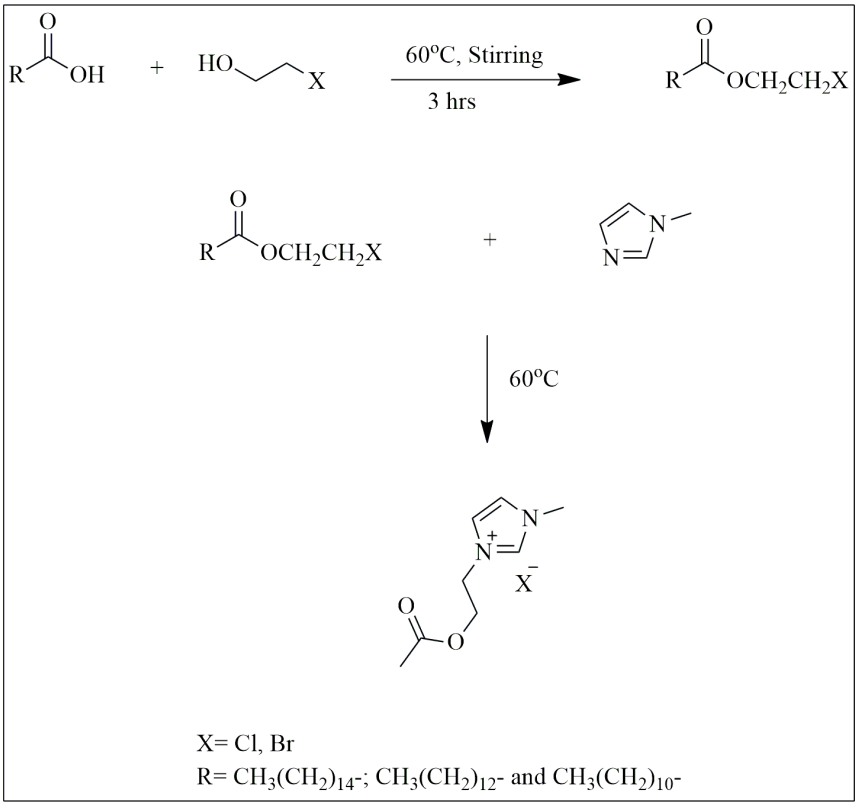
Scheme 8

Patial et al (2014) prepared novel cationic based monomeric imidazolium surfactants with epichlorohydrin and fatty alcohols which are sustainable raw materials. Epichlorohydrin was treated with alcohols and then the formed mixture was reacted with imidazole to give the intermediate product. Then, this intermediate was reacted with 1-chloropropane and 1-bromopropane for 1 hr at 60˚C which gives rise to the formation of the desired monomeric imidazolium surfactants (Scheme 9). The purest form of synthesised compounds was identified with the help of ^{1}H-NMR, ^{13}C- NMR, COSY, DEPT and mass spectroscopies. CMC of the compounds was calculated after the conductivity and surface tension measurements. The values of CMC of long hydrocarbon chain imidazolium surfactants were lower than the corresponding short chain compounds. Moreover, thermal parameters have also been calculated and showed that increase in chain length increases the thermal stability (Patial et al 2014).

Ahmad et al (2014) reported cationic imidazolium monomeric surfactants in two steps. Fatty acids were reacted with halogenated alcohols in the presence of sulphuric acid as catalyst and stirred for 2-3hrs at 60˚C. The crude products were formed as esters. In the further step, these esters were reacted with 1-methyl imidazole at 60˚C for 2 hrs and results in the formation of monomeric surfactants (Scheme 10). The surface tension as well as conductivity parameters have been measured and found that CMC values were decreasing with increasement in the hydrophobic chain lengths. The thermal stability of the compounds was up to 370˚C. Moreover, surface activity in the presence of sodium halides was checked and it was found that surfactants having counter ion of bromine have low CMC values than surfactants with chlorine counter ion (Ahmad et al 2014).



Scheme 9



Scheme 10

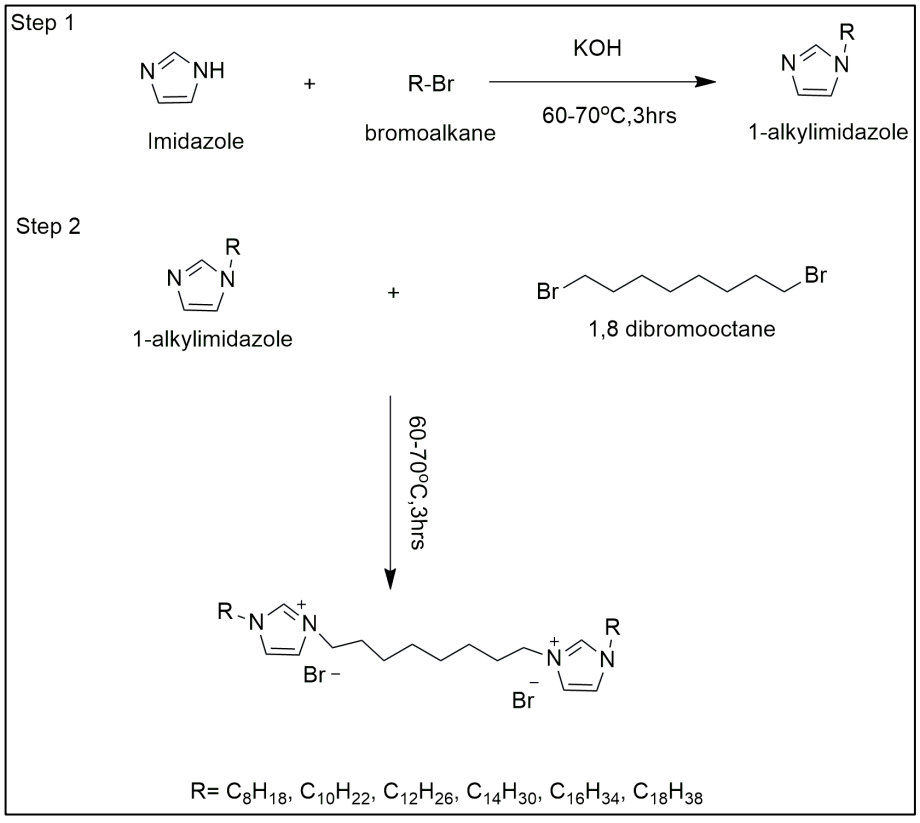
5. Technical programme

5.1 Name of the experiment: Evaluation of conductivity, interfacial properties and micellization behaviour of Imidazolium gemini surfactants.

5.2 Location of the study: Chemistry laboratory, Eternal University, Baru Sahib, Sirmaur, Himachal Pradesh.

5.3 Methodology

Synthesis: - Imidazole and KOH would be mixed in different double neck round bottom flasks and acetone would be used as solvent. The reaction mixtures would be stirred and refluxed for 3 hours at 60-70℃. Then, to each flask alkyl bromide (C_8H_{18}, $C_{10}H_{22}$, $C_{12}H_{26}$, $C_{14}H_{30}$, $C_{16}H_{34}$ and $C_{18}H_{38}$) with different chain length would be added. Each mixture would be stirred and refluxed again for 3 hours at 60-70℃. The reaction would be monitored using TLC. Each reaction would show the formation of intermediate product i.e. monomeric surfactants. Work-up would be done for recrystallization and removing excess of impurities. Further, two moles of the intermediate products would be reacted with spacer in round bottom flask at 60-70℃ for 3hours. After the completion of reaction, solvent would be evaporated and work-up would be done for recrystallization.



5.4 Observations to be recorded: Following observations will be recorded:

5.4.1 Spectral (FTIR, ^{1}H- NMR, ^{13}C- NMR) and Thermogravimetric analysis would be outsourced.

5.4.2 The conductivity of different solutions at different concentrations and temperatures would be checked by HANNAH 12300 microprocessor conductivity meter.

5.4.3 From the plots of density, viscosity and conductance vs. concentration, the values of Critical Micellar Concentration (CMC) would be calculated and CMC data will be used to derive other physical parameters.

5.5 Statistical analysis: The data collected will be statistically analysed using standard procedures for the correlation, CMC, surface-active parameters using Origin software.

6. Collaboration (if any): Nil

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